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Recent Advances in Anomalous transport models for predicting contaminants in natural groundwater systems

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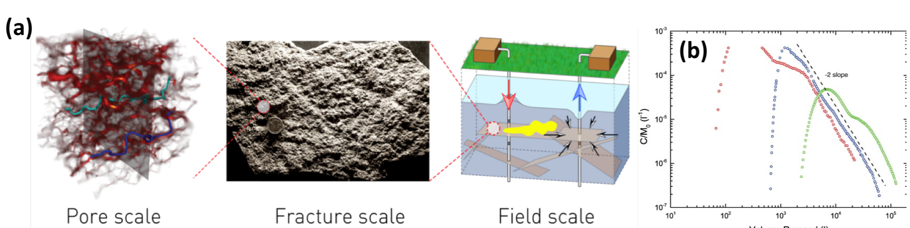
Abstract

The high spatial heterogeneity in hydrologic systems poses a major barrier for their protection and remediation. Dissolved and particulate contaminants are mixed and retained over timescales ranging from seconds to years due to their interactions with these structural heterogeneities. Over the last two decades, a new class of models has demonstrated its capacity to describe this "anomalous transport" behavior that is ubiquitous to nearly all flowing waters. The promise of these models lies in their potential for predicting transport using minimal parameters, while remaining faithful to the underlying complexity of the system. In this review, we highlight recent experimental studies that have improved our understanding of the structural controls of anomalous transport, as well as modeling studies that use these new insights to better predict contaminant fate.

Keywords:

Graphical Abstract



1. Motivation

Despite our image of Earth as the 'blue' planet, global supplies of clean water are arguably the most valuable, yet fragile, natural resources. Threats to freshwater arise from contamination by agricultural, industrial, urban, and resource mismanagement activities [36]. To minimize threats, a thorough understanding of the inherently complex structures that underpin flow and transport processes in water systems is necessary. A major challenge is that hydrologic systems are natural geologic systems with an extraordinary amount of inherent heterogeneity that is impossible to fully characterize, making predictions with high confidence difficult. While all hydrologic systems face this challenge, we will restrict our discussion to one: groundwater systems. However, many of the advances that we highlight have similar impact in other hydrologic settings such as streams and rivers.

At field scales, the most common models typically use average system quantities to define parameters for the flow equation and advection-dispersion equation (ADE). Such models serve as reasonable first estimates, but ultimately fail at capturing the extreme behaviors caused by the system's structural complexity [22]. For example, studies by the United States National Research Council [e.g. 12, 13] highlight that court ordered pump and treat strategies fail to adequately remediate polluted sites as much as 90% of the time. In many cases, failure can be attributed to designs with conventional models that do not adequately represent system complexity. Failing 9 of 10 times is unacceptable by any engineering standard. Significant limitations of conventional approaches highlight the critical need for better theories and models that accurately incorporate, or at the very least acknowledge, the presence and impact of heterogeneity and natural variability in hydrologic systems.

The specific nature of heterogeneities can vary considerably and is not clearly known in hydrologic systems. After all, classifying something as heterogeneous only indicates that it is not homogeneous, but tells us nothing about its nature [14]. In groundwater flows, it is geology and how it varies in space that causes complexity; real aquifers exhibit structure across an astonishing range of scales, from micrometer sized pores to structures on the order of tens to hundreds of kilometers. Heterogeneity comes in a variety of forms: permeability which controls how quickly water can flow can vary over many orders of magnitude depending on the material making up the aquifer; fractures and other preferential flow paths can exist that transmit water much more quickly than through the pore space in consolidated media; and geochemical heterogeneity due to spatial variability in mineral surfaces allows solutes to sorb and interact with the geologic medium over a broad range of rates. The extremely broad spatial and temporal variability in a geologic system makes it impractical to characterize it by a single effective parameter. For this reason, models like the ADE will always fail – as they are implicitly derived based on the assumption of narrow distributions and local processes. Any transport model seeking to improve the predictive capability beyond conventional models must incorporate the extremely broad range of spatial variability in a geologic systems. For these models to be useful, they should capture this complexity using a minimal set of effective parameters

2. Anomalous Transport Models

As highlighted, ADEs inherently have great difficulty in capturing observed behaviors in real hydrologic systems. Most forms of the ADE are implicitly built on the assumption of Fickian transport; that is, diffusive and dispersive mass transfer can be modeled as proportional to the concentration gradient. While, as shown in the seminal work of GI Taylor [47], this assumption may hold at asymptotic times, such timescales may be prohibitively large for practical interest. Transport that is not well described by Fickian dispersion is typically referred to as non-Fickian or anomalous. Indeed, anomalous transport is found so commonly in natural systems well beyond hydrology, that recently one of the pioneers of anomalous models argued it be renamed "ubiquitous transport" [19]. Although our discussion is restricted to the context of hydrology, it must be noted that anomalous transport models have substantially impacted other disciplines in the natural and physical sciences also [27].

One reason Fick's law makes sense and works remarkably well in certain contexts is that for a pulse initial condition, Fickian diffusion naturally results in a Gaussian concentration profile. Diffusion/Dispersion aims to represent random jumps solutes undergo due to subscale fluctuations (molecular for diffusion, velocity variation with dispersion). By the central limit theorem, such random jumps converge to a Gaussian distribution, provided jumps are independent and identically distributed (iid) with finite mean and finite variance. When solutes can make extraordinarily large jumps or be retained for very long times, this assumption becomes questionable. Convergence to Fickian behavior, while it may ultimately occur, will be at such large scales as to be irrelevant to a practitioner.

Thankfully, a rich family of models has emerged that relaxes this assumption that particle jumps follow narrow-tailed distributions. These models take advantage of ideas such as the generalized central limit theorem to still converge to analytically tractable solutions that can capture observed anomalous transport. Among these, perhaps the most popular are fractional Advection Dispersion Equations (fADE), continuous time random walks (CTRW) and multi-rate mass transfer (MRMT). It is important to note that these are certainly not the only anomalous transport models, and perhaps not even the most theoretically sophisticated (see [39] for a comprehensive discussion), but they are parsimonious and open sharing of computational toolboxes [e.g. 11, 26] has facilitated application. All of these models can also be expressed from Lagrangian and Eulerian perspectives, enabling users to have a clear physical understanding of what the models aim to represent. Although these models are very closely related, it is common to find that a user's particular choice is tightly coupled to their conceptual model of the system they are studying.

While these models have been immensely successful in capturing real world observations across diverse hydrologic settings, they are not without shortcomings, among which we point out the following:

(i) While agreement between model and measurement can be remarkably good, a common criticism is that these models are able to fit observations because of the increased number of parameters they have (for conservative transport 3-5, compared with 2). Unlike for example ADE models, it is difficult to obtain physically-motivated estimates for these model parameters, and parameter estimation often becomes a fitting exercise (i.e. transport is measured and then fit, rather than actually predicted). Linking model parameters to physical characteristics of the system at hand therefore remains a central challenge. However, characterizing hydrologic systems to this level of detail has historically been difficult, due to inaccessibility of porous media.

(ii) Most typically, the success of these models is assessed by comparing them to measured breakthrough curves (BTCs), which are concentration time series some distance downstream from an injection point. The BTC is often the only form of data that one can realistically obtain at scales of interest, but it has some implicit limitations. BTCs are an integrated measure that ultimately lumps many important processes together, making it difficult to disentangle individual controls. Experimental measurements and techniques that can help distinguish different processes will be essential to providing a more physical basis for these models.

(iii) As sophisticated as the aforementioned anomalous transport models are, they are often still built on strong assumptions. For example, while we can relax the assumption of finite mean and variance in the central limit theorem, the generalized central limit theorem still requires iid random variables. Many studies over the last decade have shown that the assumption of independence may not be adequate at the kinds of scales that practitioners are interested in, depending on the system at hand.

(iv) All of the anomalous transport models listed above use dimension reduction to predict how solutes move downstream; i.e. even though aquifers are clearly three-dimensional systems, these models are often developed in one-dimension and so any prediction that one obtains is an effective projected/mean concentration. (It is true that multi-dimensional forms of these models exist, but applications are more limited and often still typically involve some degree of reduction.) Given the integrative nature of BTCs noted above, this of course make sense: it is risky to base predictions on a model that cannot be validated by experimental measurements. However, should one be interested in more complex nonlinear processes (e.g. mixing and chemical reactions), then a prediction of mean concentration is not sufficient and more information about subscale effects is needed.

3. Advances in Anomalous Transport Models

***Improved characterization and simulation capability*:** Some of the greatest advances in our understanding of flow and transport processes over the last decade can directly be attributed to techniques that enable better (visual) access to the internal structure of porous media. Innovative technologies, including micro-CT and Nuclear Magnetic Resonance among others have enabled us to obtain three-dimensional images of the internal structure of complex real geologic porous media at a scale and resolution that was previously unobtainable [50, 41]. Similar parallel advances in computational resources have made accessible open source, state of the art computational fluid dynamics packages [e.g. 10] that simulate the complete velocity field within the imaged complex porous structures. These new simulation approaches enable calculation of useful quantities such as velocity probability distributions, which could previously only be inferred indirectly by inverse modeling of BTCs and the likes. Furthermore, flow simulations can be coupled with Lagrangian and Eulerian transport codes, enabling high-resolution simulation of transport processes, including solutes undergoing mixing-driven and heterogeneous reactions.
Highlighted Paper: A large number of papers using high resolution imaging have emerged from a research group at Imperial College London. Here we highlight one [40], which we feel demonstrates the power of these techniques. The authors develop a particle-based method to simulate dissolution reactions at pore scales using voxelized three-dimensional micro-CT images. Their approach is validated against a dynamic imaging experiment where a Ketton oolite is imaged during CO2-saturated brine injection at reservoir conditions, again exploiting advances in imaging technology [33] (see Figure 1). The model results agree well with measured changes in porosity and permeability, and the spatial distribution of the dissolution front is correctly replicated. Advances on observation enabled a physically based model capable of reproducing behavior in a highly complex setting that previously would have been entirely empirical and whose generality might be questionable.

***Improved experimental techniques*:** Similarly, experimental breakthroughs have occurred. As noted, a major limitation is our inability to directly observe and measure transport within the porous medium, thus typically ending up with integrated measures such as BTCs that do not enable direct inference of actual processes. A major breakthrough in this regard has been using refractive index matching (RIM) approaches where the fluid and the porous medium are chosen such that they have identical refractive index, rendering the solid phase transparent and allowing direct visual access to the internal flow. These advances, coupled with particle tracking velocimetry (PTV) and particle imaging velocimetry (PIV) techniques, allows for direct characterization of velocity fields.
Highlighted Paper: Here we highlight the work of Morales et al. [35] who studied the evolution of velocity in time in porous media by experimentally tracking tracer particles moving through a transparent, 3-D synthetic sandstone. Using

state of the art PTV, they measured the correlated nature of velocities along stream lines. The observed behavior is well described by a correlated CTRW model and is one of the first examples where such a model is derived from experimental rather than numerical data. The model is based on an Ornstein-Uhlenbeck [49] process to model velocity evolution and can be quite simply parameterized with the correlation length as well as the mean and standard deviation of velocity distribution, which may be obtainable in general settings. The same methods were later used to study flow evolution in a porous medium gradually invaded by biofilm [8] (Figure 3).

***Newer Models that relax previous assumptions*:** About a decade ago, Le Borgne *et al.* [29, 31] introduced a model that now goes by the name the Spatial Markov Model (SMM). It is closely related to CTRWs and fADEs, but differs in that it imposes correlation between successive jumps, relaxing the assumption of independent increments. The authors found that velocity correlations in space were sufficiently short range that successive velocities could be represented by a Markov process. They originally studied it in heterogeneous porous media at geologic scales, but since then it has been broadly shown to work well in fractured media [e.g. 23], pore scale settings [e.g. 28] and beyond. It was also shown that particles display highly intermittent behavior, alternating between quiescent periods of low velocities and small accelerations and energetic periods of large velocities and large accelerations. Such intermittent behavior necessitates a correlated model with the specific characteristics of the SMM [15]. Another promising development has been the PhEDEX model (Phase Exposure-Dependent EXchange) [20], which builds on the ideas of MRMT models. At the root of this model is the idea that solute concentration evolves with respect to two separate times: time-mobile as well as exposure time (i.e. when a particle is exposed to another process - such as immobilization). One of the main points of interest of the PhEDEX is that it casts the problem in a way that clearly separates transport and delay mechanisms. (In many other anomalous transport models these mechanisms are lumped together via complex convolutions with memory functions). This paves the way for physical parameterization of the model processes, although evidence to demonstrate these attributes is not yet experimentally available.
Highlighted Paper: Here we highlight the work of Kang et al. [25], who applied the SMM to tracer experiments in fractured media at a field site in France (see Figure 2). What stands out about this paper is that it is, to our knowledge, the first application of the SMM to field data that did not rely on high resolution numerical simulations to measure travel time distributions and parameterize correlation effects. The authors introduce a relatively parsimonious model (similar to the one used by [35] noted above) with which they successfully capture field experiment data of characteristic anomalous transport behavior in a complex real setting. This work paves the way for applications in real practical settings, which to date have not been achievable. While other approaches with real experimental data are possible [e.g. 42, 43] the parsimony of Kang et al. [25] is truly elegant and appealing.

***Upscaling in Three-Dimensions*:** As noted, dimension reduction is common for many anomalous transport models. However, the world is three-dimensional and much important information can be lost when not considering the full three-dimensional concentration field. Increasingly, authors are considering spreading in multiple dimensions [e.g. 24], but do not always consider the full coupling between longitudinal and transverse dimensions. A proper description of this coupling is necessary to capture the pronounced spatial coherence of the advective process, which strongly determines mixing behavior. Part of the challenge lies in the complexity of flow and transport, as well as in available techniques to quantify large-scale behavior in three spatial dimensions. Most et al. [37] demonstrated this by studying particle trajectories in a Doddington sandstone sample, showing transport processes are strongly correlated in all three directions such that full parameterization would require correlation descriptions using a nine-dimensional set of transition matrices. While they showed this approach to be effective, it is impractical for real porous media. Moreover, new trajectory-based methods are emerging to upscale simulated particle trajectories in a physically consistent manner [e.g. 45, 44].

Highlighted Paper: The recent paper we highlight here is Most et al. [38]. Using high resolution trajectories obtained from simulations in a Doddington sandstone, they proposed a novel training trajectory method, where trajectories are cut into small fragments that are then stitched together into much longer trajectories that ensure continuity of velocity magnitude and direction. Using this method, the authors fully reconstructed BTCs and dilution profiles obtained from much more costly direct numerical simulations. The method, inspired by training image methods in geostatistics, is in our view radically different from previous approaches and has great potential for application in other settings and at other scales that are difficult to upscale in three-dimensions.

***Connecting spreading and mixing behaviors*:** A wide range of nonlinear processes in hydrologic systems depend directly on local concentrations of interacting solutes and concentration gradients, including kinetic/equilibrium reactions and biological activity [18, 48]. Most anomalous transport models, due to dimension reduction, cannot explicitly account for concentration variations, but instead provide a measure of plume spreading and mean concentrations. While mixing and spreading are fundamentally different, recent studies show that they are tightly linked [e.g., 30], illustrating the potential to utilize existing transport theory to predict mixing and reactions. One promising advance is lamella theory, which conceptualizes a mixing interface as a line that distorts into lamellar structures as it stretches and folds in a heterogeneous velocity field [32] (see Figure 4). The lamellae eventually coalesce by diffusion, resulting in a progression through multiple mixing regimes over time. By recognizing these different processes and regimes, the lamellar framework predicts the global evolution of mixing based on limited information relating to structural heterogeneity and plume spreading characteristics. The framework has also been used to predict how chemical reactions progress in a complex porous medium [1, 16]

Highlighted Paper: We highlight Bandopadhyay et al. [4] as it is a perfect example of how advances in subsurface hydrology also help advance other areas of hydrology like the hyporheic zone and hillslopes. The authors use lamellar theory to predict mixing in flows driven by hydraulic head gradients. Head gradients form in areas of topographic relief (e.g., hillslopes, bedforms in rivers), and they generate a hierarchical structure of streamlines. Bandopadhyay et al. [4] show that these structures act as shear flows, causing a front of solutes to stretch as it propagates into the subsurface. Their predictions provide valuable insights into the formation of mixing hotspots in highly reactive subsurface regions in streams and rivers, hillslopes, and geologic formations.

4. Outlook for the Future

Improved predictions of aquifer vulnerability, remediation strategies, and human risk to groundwater contamination are defining challenges for freshwater sustainability in the 21st century [13]. This paper illustrates recent theoretical and experimental progress toward describing fundamental pore-scale processes that manifest at scales relevant to these challenges. We anticipate that near-term progress toward improved predictions will continue via development of physically-based theoretical models; leveraging continued growth of computational power, resources and tools; development and application of more sophisticated experimental techniques; improved characterization methods; and novel data driven approaches. As exemplified in our highlighted studies, we expect the parallel advancement and blending of these efforts will spur the greatest progress. While we have substantially improved the ability of anomalous transport models to accurately describe how pore-scale heterogeneity manifests at larger scales, the applicability of these models remains an open question. For example, many recent efforts are aimed at increasing our ability to measure and model small scale features that give rise to large scale anomalous transport. This has entailed gaining accurate small-scale descriptions of relevant processes, which can then be upscaled efficiently. However, an open question remains regarding the representativeness of the elementary volumes that are being studies - e.g. in pore scale studies, can an $\mathcal{O}(\mathrm{mm}^3)$ sample truly provide all the information needed to predict large scale transport in a real sandstone aquifer? The existence and size of a representative elementary volume, particularly as more complex processes are considered, is an age old problem in hydrology that is yet to be adequately resolved [e.g. 5, 9].

Nonetheless, linkage between structural controls and upscaled transport predictions will pave the way for improved mathematical descriptions of the complex feedbacks between mass transport and additional processes that ultimately determine contaminant mixing and reaction [6, 18, 48, 2], chemical weathering [21], biological growth [e.g. 8, 3], and response to large-scale environmental perturbations [e.g. 34]. Critical to improving predictive capability is an understanding of how highly detailed descriptions of transport at small scales apply to the scales where ultimately, these efforts will provide quantitative measures of human and ecosystem risk [46, 7, 17]. Such advances are sorely needed to improve the success of remediation strategies and policies designed to protect the largest fraction of freshwater resources on Earth .

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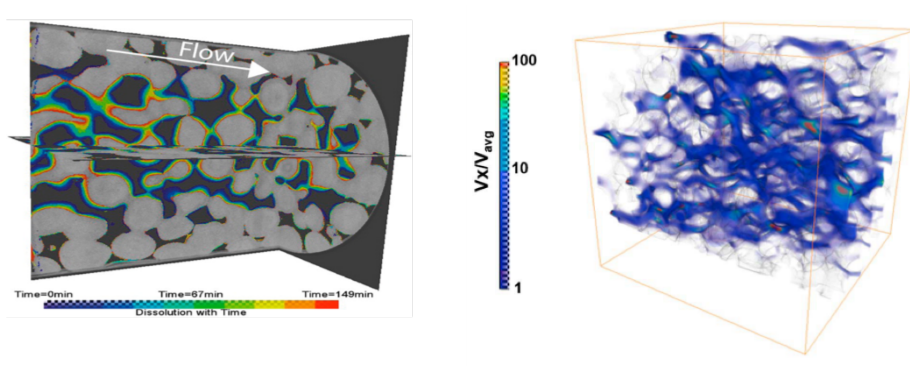

Figure 1: (Left) X-ray microtomography imaging used to study the to study the dynamic evolution of pore structure (Right) A three-dimensional segmented image of a Ketton carbonate superimposed with the simulated velocity (logarithmic color scale) along the flow direction. Taken from [33, 40].

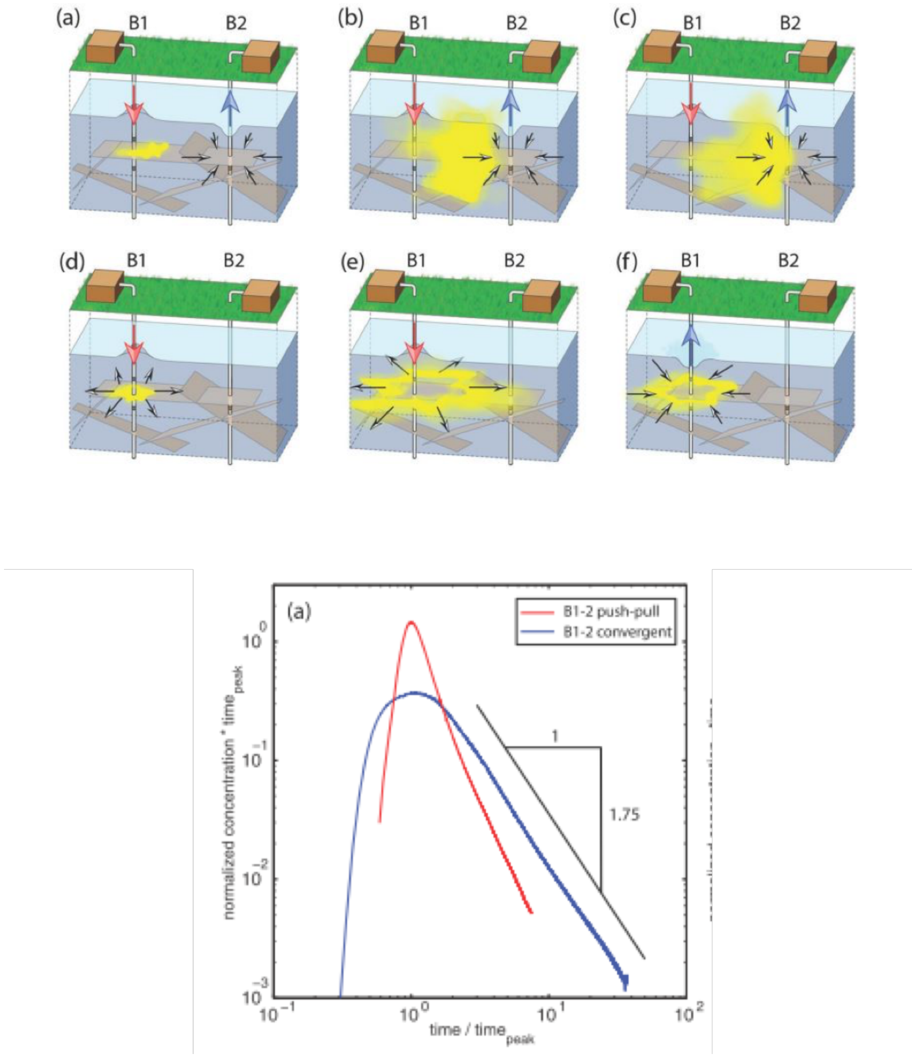

Figure 2: (Top) Schematic of the tracer tests conducted. (a,b,c) Convergent test with tracer placement at borehole B1 and pumping from bore- hole B2. Two different fracture planes at different depths (B1–2 and B1–4) are used for two separate tests. (d,e,f) Push-pull test from bore- hole B1. The same two fracture planes (B1–2 and B1–4) are used. (Bottom) Measured breakthrough curves (BTC) for the tracer tests conducted for fracture plane B1–2, in the form of a normalized time (peak arrival at dimensionless time of 1) and normalized concentration (such that the area under the BTC is identically equal to 1). Taken from [25].

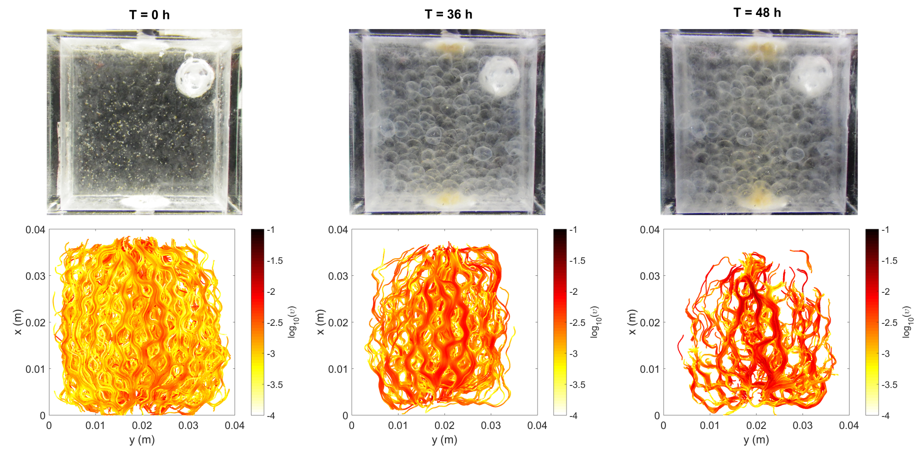

Figure 3: Photographs illustrating (top) progressive changes in the porous media with increasing bioclogging of a flow cell and (bottom) particle trajectories obtained by 3-D-PTV for three points in time. The trajectories are color coded with the logarithm of the norm of the velocity vector. Taken from [8]

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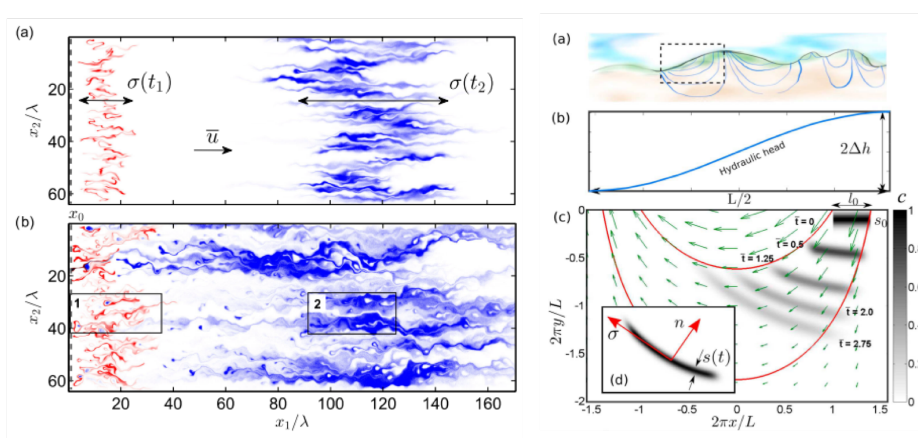

Figure 4: (Left) Concentration fields at two times (proportional to color intensity) for an initial line injection with uniform concentration in two heterogeneous porous media (bottom momore heterogeneous). The plume is transported from left to right with with a spreading scale σ clearly depicted. The lamellar structure of the plume clearly stands out. Taken from [32]. (Right) (a) Topography driven flows in the subsurface. The dotted section depicts (b) the magnified portion idealized as a sinusoidal hydraulic head. (c) An initially uniform plume of vertical width s0 containing a solute deforms into an elongated thin lamellar structure due to the differential velocity between the two representative streamlines (red lines). The plume is shown at different normalized times. Taken from [4]